
Density Functional Gaussian-Type Orbital Approach in Theoretical Study of S₂F₂ Isomerization

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ABSTRACT

The structures of two isomers, difluorodisulfane (FSSF) and thiothionylfluoride (SSF₂), and the corresponding transition structure were generated with density functional theory (DFT) methods. Three groups of DFT methods were used: local (Local Spin Density Approximation, LSDA), nonlocal (local with gradient corrections; BLYP and BP86), and hybrid methods that include a mixture of Hartree-Fock (HF) exchange with nonlocal correlation (Becke3BLYP, Becke3P86). An extended basis set [6-311++G(3df)] was used for all calculations, although satisfactory results can be obtained with the 6-311G(d) basis set. The geometries obtained were compared with both restricted Hartree-Fock (RHF) calculated and experimentally obtained values. The energy outcome and the activation barrier for the isomerization were evaluated. It was determined that excellent geometries can be obtained with the Becke3B86 hybrid method, whereas for reasonable energies MP2 single-point calculations on these geometries are necessary.
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Introduction

Density functional theory (DFT) offers a promising alternative for cases in which Hartree-Fock (HF) calculations cannot provide satisfactory results.¹ Furthermore, DFT methods are undoubtedly less expensive to conduct than the current *ab initio* quantum chemistry methods.² Although supporting evidence exists for the implementation of DFT methods for commonly explored

compounds and transition structures, relatively little is known regarding the application of these systems.³ Scuseri successfully applied the Becke-Lee-Yang-Parr (BLYP)⁴ DFT method for computing the pathological quantum chemistry problem, F + H₂ → FH + H.⁵ Excellent agreement for the barrier and exothermicity of the reaction with experimental results was observed. Similar agreement was obtained by DFT methods for activation energies of ethylene addition to cyclopentadiene and 1,3-butadiene.⁶ We have recently demonstrated the usefulness of DFT methods for deter-

mining the structures of several difficult computational problems, such as NO dimer⁷ and F_2NNF_2 .⁸ The DFT methods show superiority over RHF *ab initio* calculations and produce results that are equal in quality to the Møller-Plesset (MP) calculations. In this article, we present results for S_2F_2 isomers, species that are particularly difficult to compute with semiempirical⁹ and *ab initio*¹⁰ methods.

Computational Methods

All calculations were performed with the Gaussian 92¹¹ implementation of DFT with the 6-311++G(3df) basis set. The optimizations were performed without any geometric restrictions using the Fletcher-Powell¹² method and the default Gaussian convergence criteria.

In the study of the S_2F_2 isomers, the transition structures and corresponding energies of a family of standard Gaussian 92 DFT methods, including local, nonlocal, and gradient-corrected methods, were used. These methods include the following: restricted Hartree-Fock (RHF); self-consistent fields¹³; second-order Møller-Plesset (MP2) perturbation theory¹⁴; Slater exchange functional with Vosko, Wilk, and Nusair correlation functional (SVWN)¹⁵; Becke's exchange with Lee, Yang, and Parr correlation functional (BLYP)⁴; Becke's exchange with Perdew's gradient-corrected functional (BP86)¹⁶; Becke's three-parameter exchange

with Lee, Yang, and Parr correlation functional (Becke3LYP); and Becke's three-parameter exchange with Perdew's gradient corrected functional (Becke3P86).

Results and Discussion

An interesting problem in sulfur fluoride chemistry is the structure and stability of difluorodisulfane (FSSF) and thiothionylfluoride (SSF_2) and the activation energy of their interconversion. The structures¹⁷ of these two structural isomers and their energy¹⁸ difference are known experimentally. The extremely short sulfur bond lengths cannot be explained satisfactorily. Both semiempirical⁹ and RHF *ab initio*¹⁰ calculations do not predict correct structural characteristics and the relative energy of the reaction. Our results of geometric characteristics of difluorodisulfane are presented in Table I.

The RHF/6-311++G(3df) *ab initio* theoretical model has a problem in estimating both SS and SF bond distances. They differ by 0.047 Å and 0.036 Å from the experimental data and are roughly four times larger than the experimental error. In addition, the SSF has a bond angle difference of 2.5°. The RHF method, even with the extended basis sets, is not suitable for modeling systems that have considerable charge separations, like the ones presented here. Three groups of DFT methods were used for the computation of the S_2F_2 isomers.

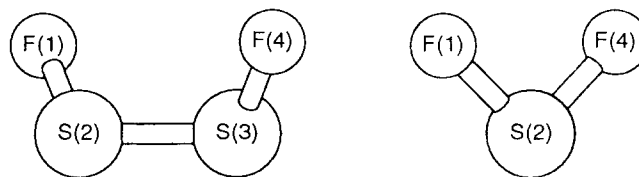


TABLE I.
Geometric Parameters and Total Energy (au) of Difluorodisulfane Calculated with the 6-311++G(3df) Basis Set.

Method	112	123	a123	d1234	Total energy
RHF	1.588	1.924	106.0	86.6	-993.98542
SVWN	1.647	1.871	109.8	87.2	-993.20928
Becke3LYP	1.656	1.899	108.6	86.8	-996.18192
Becke3P86	1.643	1.886	108.8	87.0	-997.09397
BLYP	1.701	1.910	109.8	87.0	-996.15764
BP86	1.683	1.896	110.0	87.0	-996.24685
RHF / Becke3P86					-993.98113
MP2 / Becke3P86					-994.83644
SVWN / Becke3P86					-993.20914
Experimental ¹⁷	1.635 ± 0.01	1.888 ± 0.01	108.3 ± 0.5	87.9 ± 1.5	

They are local (SVWN) hybrids (Becke3LYP and Becke3P86) and nonlocal (BLYP, BP86) DFT methods. SVWN/6-311++G(3*df*) predicts the geometry of FSSF well. The SS bond distance is 0.012 Å away from the experimental value, with an experimental error of ± 0.01 Å. The same accuracy is predicted for the SF bond distance. It is only 0.011 Å away from the experimental value with the same experimental error. Therefore, the prediction of the SSF bond angle is slightly less accurate. Its deviation from the experimental value of 1.5 Å is three times larger than that of the experimental error. Surprisingly, the dihedral angle for this and all other calculations is in excellent agreement with the experimental value. This agreement, obtained by the local SVWN DFT method, is not so surprising. In our theoretical study of the NO dimer with the SVWN method, it was found that the geometric parameters are similar to the experimental data.⁷

The hybrid methods generated by our results with the FSSF structure concluded that it was closest to the experimental geometry of all applied DFT methods. Of the two hybrid methods, the Becke3P86 gives a preferred geometry. The SS distance was pointed out to be extremely difficult to determine computationally⁹ because it was only 0.008 Å away from experimental value, which is within the 0.01 Å experimental error. The predicted SF bond deviates a mere 0.002 Å from the experimental value. Similarly, the predicted bond angle and dihedral angle of the experimental

structures are smaller than experimental error. Another hybrid method, Becke3LYP, generated comparable results to SVWN, even though it was not shown to be as close to the experimental value as the Becke3P86 method.

We conclude from our findings that both non-local DFT methods, BLYP and BP86, poorly predict the SS bond distance. The predicted values are 0.066 Å and 0.048 Å away from the experimental values for BLYP and BP86, respectively. This prediction is an improvement over the *ab initio* RHF method; however, it is inferior to both of the local and hybrid methods applied here.

The problems present in predicting difluorodisulfane do not apply to the prediction of the structural parameters for thiothionylfluoride, SSF₂. The SS bond distance is well represented for both RHF *ab initio* methods and DFT methods (Table II). All of the methods predict that the angles are within the range of the experimental error. The major problem in computing the SSF₂ structure lies in correctly determining the SF bond distance. The RHF/6-311++G(3*df*) method underestimates the SF distance by 0.048 Å, and the problem is present in all three DFT methods considered here. For example, SVWN/6-311++G(3*df*) overestimated the SF bond distance by 0.025 Å. The results are of better quality than those produced by RHF but still are far from the desired agreement with experimental values. As in the case of the difluorodisulfane structure, the best agreement

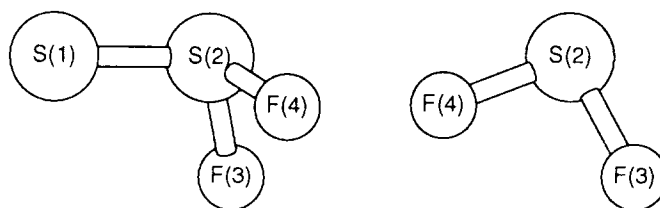


TABLE II.
Geometric Parameters and Total Energy (au) of Thiothionylfluoride Calculated with the 6-311++G(3*df*) Basis Set.

Method	112	123	a123	a324	Total energy
RHF	1.860	1.550	108.1	91.7	-993.98099
SVWN	1.854	1.623	107.7	91.7	-993.21230
Becke3LYP	1.866	1.632	108.0	91.9	-996.18035
Becke3P86	1.856	1.617	108.0	91.8	-997.09390
BLYP	1.884	1.681	108.1	92.6	-996.15581
BP86	1.876	1.661	108.0	92.4	-996.24642
RHF / Becke3P86					-993.97582
MP2 / Becke3P86					-994.84555
SVWN / Becke3P86					-993.21171
Experimental	1.860 \pm 0.015	1.598 \pm 0.012	107.5 \pm 1	92.5 \pm 1	

with experimental data was observed with hybrid methods, particularly with Becke3P86/6-311++G(3df). The structural parameters for this method are only 0.004 Å for SS, 0.019 Å for SF, 0.5° for SSF, and 0.7° for FSF away from experimental values.¹⁷ As in the previous case, the generated structures with nonlocal DFT methods overestimate the SF bond distance by more than 0.06 Å (Table II). Thus, we have demonstrated again that both of the hybrid methods provide results which are closer to experimental data than the RHF, local, or nonlocal DFT methods.

The structural parameters for the transition state of the fluorine-1,2 shift that transmutes difluorodisulfane into thiothionylfluoride are presented in Table III. It is not possible to estimate the validity of DFT calculations for this transition structure because the experimental data are not available for any transition structure. We can only assume that the methods which produced the structures for the two isomers will give the most accurate transition structure and the corresponding activation energies, as was demonstrated, for the Diels-Alder and polar pericyclic reactions. For rearrangement of the SF₂—SF₄ three-membered ring, the transition structure is considered to be the most likely structure. For both isomers we have demonstrated that computing the SS and SF

bond distance is difficult. In the transition structures there is an additional problem in calculating the bonds that are forming and breaking, because the SF bond distance is difficult to compute. Therefore, the problem of bond forming and breaking is even more pronounced. It appears that the local SVWN predicts a more compact structure, whereas the nonlocal BLYP predicts an enlarged geometry. As mentioned earlier, we believe that the closest structure to the real transition state should be the one obtained by the Becke3P86 hybrid DFT method. The generated structure lies between those predicted by the nonlocal and local DFT methods (Table III).

The heat of transformation of difluorodiazete to thiothionylfluoride is determined experimentally as 2.7 ± 0.5 , but to the best of our knowledge the activation energy for this reaction is not known. As in many previous cases, when the computation of difficult problems is investigated by the RHF method, the wrong isomer is preferred.^{7,8} The reaction is predicted to be endothermic (Table IV). To our surprise, the nonlocal³ and hybrid DFT methods that usually predict correct energies also favor endothermic reactions, except for Becke3BLYP, which predicts equal energy for both isomers. In fact, only the local SVWN of all DFT methods studied here predicts the transformation

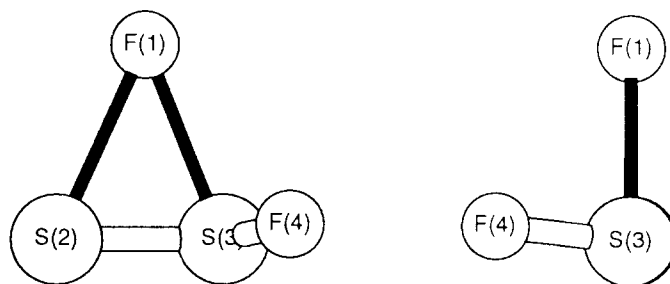


TABLE III.
Geometric Parameters and Total Energy (au) of the Transition Structure with the 6-311++G(3df) Basis Set.

Method	112	113	123	134	a213	a234	a134	Total energy
RHF	2.300	2.254	1.792	1.538	46.3	109.8	91.7	−993.87040
SVWN	2.224	2.221	1.826	1.607	48.5	110.3	95.6	−993.13914
Becke3LYP	2.294	2.272	1.833	1.615	47.4	110.2	96.7	−996.10685
Becke3P86	2.264	2.247	1.823	1.603	47.7	110.2	96.0	−997.01554
BLYP	2.332	2.320	1.857	1.660	47.0	110.8	99.6	−996.09421
BP86	2.298	2.289	1.847	1.643	47.5	110.8	98.3	−996.17978
RHF / Becke3P86								−993.86733
MP2 / Becke3P86								−994.76763
SVWN / Becke3P86								−993.13913

TABLE IV.
Relative and Activation Energy (kcal/mol) for FSSF Transfer to SSF₂ with 6-311++G(3df).

Theoretical model	$\Delta E = E_{\text{FSSF}} - E_{\text{SSF}_2}$	$\Delta E = E_{\text{TS}} - E_{\text{FSSF}}$
RHF	2.8	69.4
SVWN	-1.9	45.9
Becke3LYP	1.0	46.1
Becke3P86	0.0	49.2
BLYP	1.1	38.6
BP86	0.1	41.9
RHF / Becke3P86	3.3	68.1
MP2 / Becke3P86	-5.7	48.9
SVWN / Becke3P86	-1.6	45.5
Experimental ¹⁸	-2.7 ± 0.4	

of FSSF to SSF₂ as 1.9 kcal/mol exothermic. The deviation from experimental values is twice that of the experimental error. With an eye toward improving the experimental correlation of the predicted energy, single-point calculations on the geometries that are produced by Becke3P86 and closest to the experimental structures were performed. As expected, the RHF single-point calculation on correct geometries again prefers the wrong isomer. MP2 calculations overestimate the energies and predict the reaction to be exothermic, with energy roughly twice that of experimental value (Table IV). SVWN single-point energy actually gives poorer results than full SVWN/6-311++G(3df) calculations.

For the activation energy, it is difficult to determine the actual values because experimental data are not available. All DFT methods seem to agree that this value has to be somewhere between 40 and 45 kcal/mol, countering the notion that the FSSF is not stable and readily isomerizes to SSF₂.¹⁹

Conclusion

It was demonstrated that the RHF *ab initio* method, even with an extended basis set like 6-311++G(3df), cannot correctly predict either geometric parameters or the energy of polar compounds like FSSF and SSF₂. The DFT-generated structures, with the local (SVWN), nonlocal (BLYP, BP86), and hybrid (Becke3LYP, B3P86) methods, produced structures that are in much better agreement with the experimental data. The best method employed in this study was Becke3P86, which produced structures of both isomers that are different from experimental results by less than experimental error. Unfortunately, the energies pre-

dicted with DFT methods are not indisputably superior. Most of them, such as the RHF *ab initio* method, prefer the wrong isomer; this is a problem that can be partially corrected by MP2 energy evaluation of Becke3P86 geometries.

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